LEVEL II

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NON-CARCINOGENIC REPLACEMENTS FOR PBNA ANTIOXIDANT IN PBXN-105 AND PBXN-106 EXPLOSIVES

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NWS

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Explosive mixes of PBXN-105 and PBXN-106 were prepared using Cyanox 2246 and CAO-14 antioxidants in lieu of phenyl-beta-naphthylamine (PBNA). Specification tests, as well as other related tests, were performed on the system. Findings indicate either of the antioxidants are suitable replacements.

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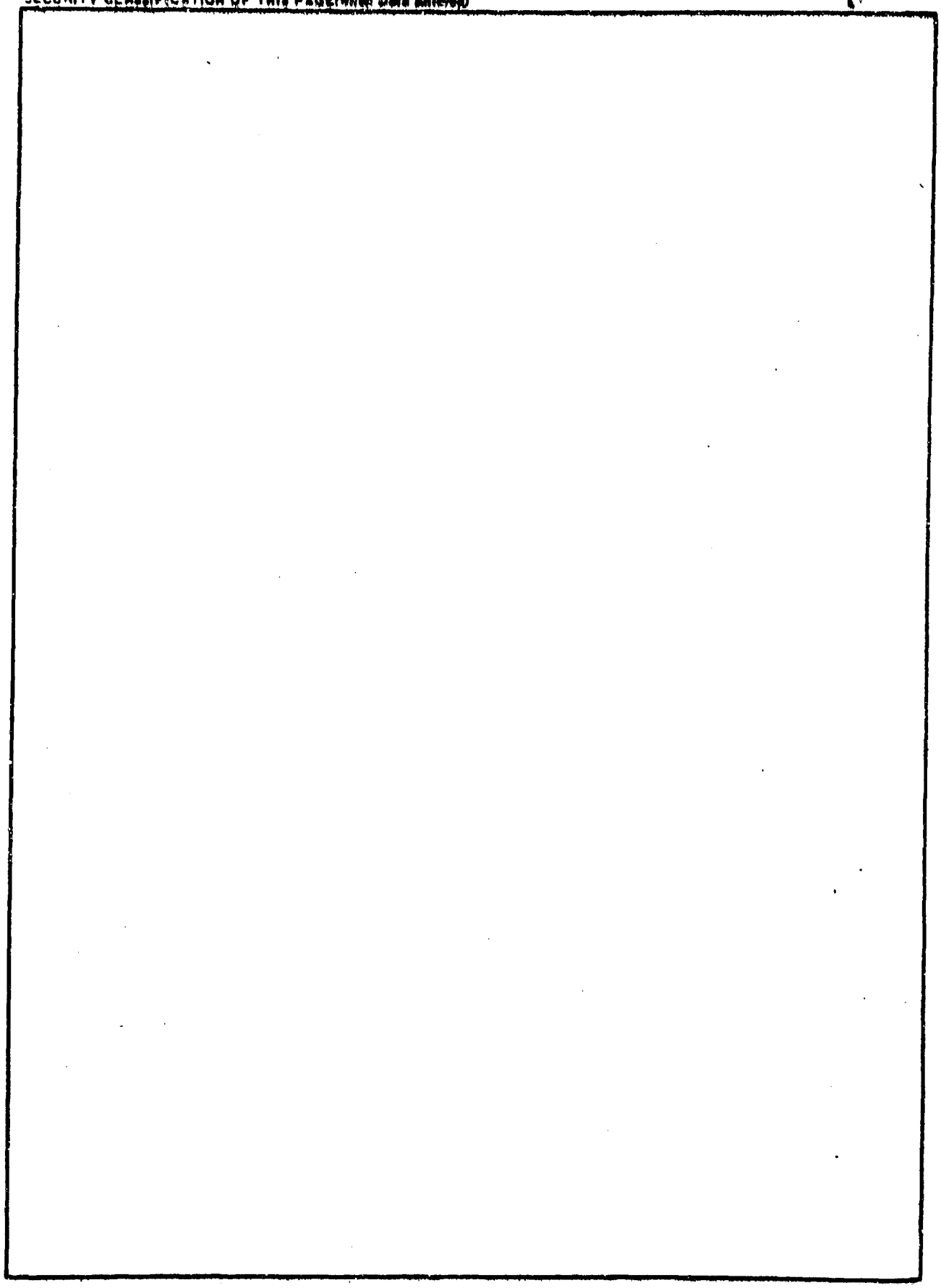

F O R E W O R D

1. This report describes the tests performed to determine the feasibility of replacing carcinogenic phenyl-beta-naphthylamine (PBNA) in PBXN-105 and PBXN-106 with alternate antioxidants.

2. The effort reported herein was authorized and funded under the Naval Sea Systems Command Work Requests WR9C054 of 1 October 1978 and WR9G464 of 11 June 1979.

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NON-CARCINOGENIC REPLACEMENTS FOR PBNA ANTIOXIDANT IN PBXN-105 AND PBXN-106 EXPLOSIVES

I. INTRODUCTION

Phenyl-beta-naphthylamine (PBNA) is used in the polyurethane explosive systems PBXN-105[1] and PBXN-106[2] as an antioxidant. PBNA has been identified as a suspected carcinogen,[3] [4] creating handling and procurement difficulties.

According to the National Institute for Occupational Safety and Health, PBNA is metabolized in the human body to B-naphthylamine, a known human carcinogen.[5] All U.S. manufacture of PBNA has been discontinued; however, the material is available from foreign sources.[6] The British dispute the reported effects of PBNA because of evidence that workers exposed to the chemical had no greater incidences of bladder cancer than did the population as a whole.

Evidence to date indicates non-carcinogenic antioxidants are available. One, Cyanox 2246,[7] chemically 2,2' Methylene bis-(4-methyl-6-tertiary butylphenol), is permitted by the Food Additives Regulations as a component in food packaging adhesives and as a component in rubber articles intended for repeated use in contact with food. It is also being used

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[1] WS 13112D, "Explosive, Plastic-Bonded, Cast, PBXN-105 (U)," 3 Mar 1970 CONF.

[2] WS 13522E, "Explosive, Plastic-Bonded, Cast, PBXN-106 (U)," 22 Jan 1971 CONF.

[3] NAVSWC White Oak ltr WR-12:MJS:jdk 8010 Ser 793 dtd 17 Feb 1977 to NAVSEASYSCOM (SEA-04H3).

[4] M.I. Fauth, NSWC/WOL MP 78-19, "Alternate Sources for Propellant Ingredients," 30 Oct 1978.

[5] "Chemical and Engineering News Concentrates," Vol 55, No. 1, p. 7, 3 Jan 1977.

[6] Chemical Propulsion Information Agency, CPIA 274, "Solid Propellant Ingredient Availability Survey," Jun 1978 (Supplement to Ingredient Survey, p. 3).

[7] Technical Bulletin C-144, "Plastanox 2246 Antioxidant," American Cyanamid Co., Intermediate Dept., Bound Brook, NJ, 9-2457-500-12/69 (Rev) 300-3/70.

in PBXW-108[8] and PBXW-109.[9] This chemical is available from more than one manufacturer; for instance, the antioxidant, CAO-14,[10] is apparently a purer form of the same material.

A series of PBXN-105 and PBXN-106 laboratory batches were prepared and analyzed to evaluate the use of Cyanox 2246 or CAO-14 in lieu of PBNA. Tests were run on patties from the batches immediately after curing, and at completion of the 28-day, WR-50[11] temperature cycling. Tests will be performed on duplicate patties after one year of storage in laboratory and magazine environments. Results show no indication of problems arising from the substitution of either of the non-carcinogenic antioxidants.

II. EXPERIMENTAL

A. Equipment and Materials

A Baker-Perkins vertical, planetary mixer, size 2PX, with variable speed electrical drive and a nominal working capacity of 1 pint was used to prepare the batches. The raw materials were production grade ingredients and were obtained from local storage. A listing of these materials is given in Table I.

B. Mixing Procedures

The PBXN-105 batches were prepared by weighing all of the binder ingredients into a glass container, melting at 70 degrees Celsius (°C) and adding them to the kettle which had previously been heated to 65°C (batch temperature 60°C) and charged with the coated RDX and aluminums. This mix was agitated at slow speed (16 revolutions per minute [rpm] as measured on vertical shaft between gear box and top of kettle) for 15 minutes under approximately 7 millimeters of mercury (mm of Hg), absolute pressure. One-half of the ammonium perchlorate was added and agitated for 5 minutes at fast speed (28 rpm) and under 7 mm of Hg, absolute pressure. The remaining ammonium perchlorate was then added and agitated an additional 5 minutes as before. The 2,4-2,6-toluene diisocynate (TDI) was added and agitated for 15 minutes at fast speed under vacuum.

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[8] WS 19295, "Explosive, Plastic-Bonded, Cast, PBXW-108(I) (U)," Proposed 15 Jul 1976 CONF.

[9] H. Heller, NOL White Oak, 11 Sep 1974, private communication.

[10] Technical Data, Ashland CAO-5 and CAO-14 Antioxidants, "Antioxidants for Petroleum Products, High Polymers, Latex and Rubber," Ashland Chemical Co., Div. of Ashland Oil, Inc., Columbus, OH, Apr 1974.

[11] NAVSEA WR-50, "Warhead Safety Tests, Minimum for Air, Surface and Underwater Launched Weapons (Excluding Mine and Nuclear Warheads)," 13 Feb 1964.

The PBXN-106 batches were made by weighing all of the binder ingredients into a glass container and melting at 70°C and adding them to the kettle which had previously been heated to 65°C and charged with the precoated RDX. The ingredients were mixed at slow speed (16 rpm) for 30 minutes under 7 mm of Hg, absolute pressure. The TDI was added and mixed for 15 minutes under previously stated conditions.

C. Test Procedures

The explosive systems were tested to ensure comformance with respective specification requirements. Additional tests were also performed, such as the WR-50 JAN temperature cycle, shelf life (magazine and laboratory environments), differential thermal analysis, impact sensitivity, and relative long-term stability.

For the WR-50 JAN temperature cycle, the patties were cycled between an oven at 71.0° ± 0.5°C and a freezer at -54.0° ± 0.5°C over the test period. They were held for 24 hours at one temperature, then transferred to the other. The patties were weighed at the beginning and at the end of the 28-day period. Specification test, impact sensitivity, differential thermal analysis, and relative long-term stability studies were performed on the patties.

Specimens from the patty samples were impact tested by the Bruceton Method to obtain the 50 percent height[12] on an NOL machine using Type 12 tools with a 2.5 kilogram weight. Twenty-five trials were run using 35 ± 2-milligram (mg) samples placed on 5/0 sandpaper.

Differential thermal analysis was performed on the patty specimens using a Stone DTA, Model 23. Twenty-mg samples were heated at 10°C per minute to complete decomposition.

Shelf life samples were prepared for magazine and laboratory storage. Two patties from each batch were placed in 1/2-pint, cardboard containers, to protect them from exposure to light. One patty from each batch was enclosed in an essentially airtight metal can and placed in a magazine where temperature and humidity are uncontrolled. The duplicate patties from each batch were enclosed in a sealed, glass container and kept in the laboratory under controlled temperature and humidity. After one year, the patties will be specification tested.

[12] Rept. No. 101.1R, SRG-P No. 40 "Statistical Analysis for a New Procedure in Sensitivity Experiments," Applied Mathematics Panel of the National Defense Research Committee, 350 Fifth Ave., New York, NY, circa 1942.

The relative long-term thermal stability was determined in accordance with a procedure developed by Waldrep.[13] The method measures the storage half-life of explosives, based on reaction kinetics, as determined by a differential thermal analysis method in which specimens are heated at several heating rates to decomposition. The peak exotherm temperatures are plotted and the explosive half-life is calculated from the slope of the plotted peak exotherm temperatures.

III. RESULTS AND DISCUSSION

A. Specification Test

Results of specification test tabulated in Table II, which includes Shore A hardness, density, and vacuum thermal stability, before and after the WR-50 JAN temperature cycle, indicate no adverse reactions in either of the two systems tested.

B. Impact Sensitivity and Relative Long-term Thermal Stability

Impact sensitivity and relative long-term thermal stability results are tabulated in Table III. Data before and after the WR-50 JAN temperature cycle place the impact sensitivities in the normal range for the explosive systems. The relative long-term thermal stability determinations are considered to be checks although there are minor differences in reported values. The exponent of 10 is taken to be the determining factor in predicting the half-life of the system. The PBXN-106 batches made with antioxidants seemed to improve somewhat in relative stability after cycling, possibly due to enhanced curing or consumption of the antioxidant. The batch without any antioxidant is apparently a bit more stable before cycling than those with antioxidants, but all have about the same stability after cycling. The antioxidants are added to preserve the polyurethane binder. The apparent negative effect of the antioxidants on the RDX stabilty is supported by the vacuum compatibility tests discussed later.

C. Differential Thermal Analysis

Differential thermal analysis of PBXN-106 and PBXN-105, tabulated in Tables IV and V, respectively, exhibit no problems arising from the substitution of the antioxidants. The minor differences in decomposition temperatures are not considered to be of significance.

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[13] P. G. Waldrep, NWSY TR 79-2, "A Proposed Method for Determining the Relative Thermal Stability of Some Explosive Formulations," in press.

D. Vacuum Thermal Compatibility

Vacuum thermal compatibility results, tabulated in Table VI, reveal significant differences in reactivity gas volumes as well as evidence of physical and/or chemical changes in the systems. Although all of the antioxidants exhibit some adverse reaction due to the higher concentration of antioxidant to explosive (1:1), PBNA is clearly more reactive than the proposed replacements. The questionable compatibilities are not considered a problem, however, because of the low levels of antioxidant normally used in the systems. As indicated in Table II, the vacuum thermal stability of the explosive batches were within specification requirements.

IV. CONCLUSION

The data collected indicate either American Cyamid Cyanox 2246 or Ashland Chemical CAO-14 can be substituted for PBNA. The advantages of replacing PBNA with one of the other antioxidants are twofold. First, and most important, is the elimination of a possible carcinogen in the system, and secondly, product procurement is simplified, as Cyanox 2246 and CAO-14 are readily available in the United States, thus eliminating purchases from foreign sources as is the case with PBNA.

TABLE I. BATCH MATERIALS

Materials	Spec	Manufacturer	Comments
Syn-cyclotrimethylene Trinitramine (RDX)	MIL-R-398C Type B, Class A & E	Holston	-
Bis(2,2-dinitropropyl) Acetal Bis(2,2-dinitropropyl) Formal 50/50 Mixture (BDNPF/A)	WS 1141A	-	XB 9/7
Polyoxyethylene Gycol (PEG 4000)	WS 13110A	Dow Chemical	Lot B-197
1,1,1-Tris(Hydroxymethyl) Propane (TMP)	WS 1030A	Celanese	Lot 7509 BT
Phenyl beta-naphthylamine (PBNA)	OS 9412B	DuPont	Lot 92
Ferric Acetylacetonate (FeAA)	OS 9804A	Chemical Procurement Lab	F-0065
2,4-Toluene Diisocyanate (TDI)	OS 9405A	Mobay	E-002-4-223 TDS-80 (80/20 Isomer)
Dibutyl Tin Dilaurate (DBTDL)	WS 14418	Dow Corning	164-6150-74
Ammonium Perchlorate (AP)	WS 12794 with modifications*	Kerr McGee	Lot 5094
Aluminum	WS 12795	Reynolds	Lot 9835
Aluminum (H-5)	MIL-A-23950A(AS)	Valley	Lot 011
Cyanox 2246	In prep	American Cyanamid	Lot 7991
CAO-14	None	Ashland Chemical	Sample

*Modifications per NAVSWC White Oak ltr WR-12:HH:tac 4200 Ser 3527 of 28 Jun 1976.

TABLE II. RESULTS OF SPECIFICATION TEST BEFORE AND AFTER JAN CYCLE[a]

Antioxidant	Shore A hardness		Density (g/cc)		VTS[b] (ml/g)	
	Before	After	Before	After	Before	After
PBXN-106:						
PBNA	44	44	1.66	1.65	0.2	0.2
Cyanox 2246	30	29	1.66	1.62	0.4	0.1
Cyanox 2246[c]	40	44	1.65	1.64	0.2	0.1
CAO-14	40	44	1.65	1.64	0.1	0.1
None	39	45	1.65	1.64	0.2	0.2
PBXN-105:						
PBNA	58	71	1.92	1.91	0.3	0.2
Cyanox 2246	68	79	1.91	1.91	0.2	0.2
Cyanox 2246[c]	66	79	1.91	1.92	0.3	0.2
CAO-14	71	81	1.92	1.91	0.3	0.1

[a]WR-50 JAN temperature cycle: 24-hr cycle, between oven at 71.0° ± 0.5°C and freezer at -54.0° ± 0.5°C over the 28-day test period.
[b]Vacuum thermal stability: ml/g/48 hrs/100°C/STP.
[c]Duplicate batch.

TABLE III. IMPACT SENSITIVITY AND RELATIVE LONG-TERM THERMAL STABILITY BEFORE AND AFTER JAN CYCLE[a]

Antioxidant	Impact sensitivity[b] (cm)		Relative long-term thermal stability (years)	
	Before	After	Before	After
PBXN-106:				
PBNA	44.0	44.0	5.00×10^4	1.64×10^5
Cyanox 2246	41.9	41.5	2.17×10^4	3.31×10^5
CAO-14	40.5	41.1	1.47×10^4	1.35×10^5
None	41.1	41.5	2.91×10^6	3.35×10^5
PBXN-105:				
PBNA	13.7	13.5	1.56×10^1	2.72×10^1
Cyanox 2246	13.4	13.2	2.66×10^1	1.62×10^0
CAO-14	13.4	13.3	2.63×10^1	2.63×10^1
Std. RDX[c]	25.4	-	-	-

[a]WR-50 JAN temperature cycle: 24-hour cycle, between oven at 71.0° ± 0.5°C and freezer at -54.0° ± 0.5°C over the 28-day test period.

[b]50% ht: Bruceton Method/NOL Machine/Type 12 tools/2.5 kg wt/ 25 trials/35 ± 2 mg/ 5/0 sandpaper.

[c]Standard RDX, Class A, Holston Lot 21-50, Batch 4RCA-135, Jan 1968.

TABLE IV. DIFFERENTIAL THERMAL ANALYSIS[a] OF PBXN-106 LAB BATCHES BEFORE AND AFTER JAN CYCLE[b]

Antioxidant	Endotherm[c] range (°C)		Exotherm[d] ignition (°C)	
	Before	After	Before	After
PBNA	164-206	160-204	206	204
Cyanox 2246	163-202	156-202	202	202
Cyanox 2246[e]	163-200	158-200	200	200
CAO-14	173-204	160-202	204	202
None	163-201	164-200	201	200
Std. RDX[f]	187-215	-	215	-

[a]Stone Model 12A Thermal Analyzer: heating rate 10°C/min; sample wt 2 mg.
[b]WR-50 JAN temperature cycle: 24-hour cycle, between oven at 71.0° ± 0.5°C and freezer at -54.0° ± 0.5°C over the 28-day test period.
[c]RDX melting.
[d]RDX decomposition.
[e]Duplicate batch.
[f]Standard RDX, Class A, Holston Lot 21-50, Batch 4RCA-135, Jan 1968.

TABLE V. DIFFERENTIAL THERMAL ANALYSIS[a] OF PBXN-105 LAB BATCHES BEFORE AND AFTER JAN CYCLE[b]

Antioxidant	Endotherm (°C)		Exotherm (°C)		
	Range[c] 1	Range[d] 2	Steps[e]	Peak[f]	Ignition[g]
PBNA	167-177	241-254	177 197 222	310	339
PBNA[h]	162-172	242-254	172 200 224	306	344
Cyanox 2246	159-172	244-254	172 197 222	310	342
Cyanox 2246[h]	160-170	242-254	170 198 222	308	344
Cyanox 2246[i]	162-172	244-256	172 197 221	312	341
Cyanox 2246[h i]	156-166	244-254	166 198 222	310	336
CAO-14	160-172	244-256	172 197 221	312	343
CAO-14[h]	162-174	244-254	174 198 224	312	338
NH_4ClO_4[j]	-	244-259	-	307	338

[a]Stone Model 12A Thermal Analyzer: heating rate 10°C/min; sample wt 2 mg.
[b]WR-50 JAN temperature cycle: 24-hour cycle, between oven at 71.0° ± 0.5°C and freezer at -54.0° ± 0.5°C over the 28-day test period.
[c]Minor.
[d]NH_4ClO_4 crystalline transition.
[e]RDX melting, BDNPF/A, RDX decomposition.
[f]NH_4ClO_4 decomposition (first stage).
[g]Final decomposition.
[h]After WR-50 JAN cycle.
[i]Duplicate batch.
[j]Kerr McGee AP, Lot 5094.

TABLE VI. VACUUM THERMAL COMPATIBILITY[a]

Specimen	PBXN-106		PBXN-105	
	Reactivity[b] (ml/g)	Code[c]	Reactivity[b] (ml/g)	Code[c]
Explosive cured + PBNA	2.2	C	1.4	B
Explosive cured + Cyanox 2246	1.8	B	0.0	A
Explosive cured + CAO-14	1.4	B	0.3	A
Explosive uncured + PBNA	2.1	C	1.6	B
Explosive uncured + Cyanox 2246	1.0	B	0.0	A
Explosive uncured + CAO-14	0.3	B	0.0	A

[a]NAVORD OD 44811 Vol. I, Jan 1972.
[b]Reactivity: ml/g/48 hrs/100°C/STP.

[c]Reactivity Codes:

A = Compatible (gassing less than 2 ml/g with no evidence of physical or chemical change).

B = Questionable (gassing less than 2 ml/g but evidence of physical or chemical change).

C = Incompatible (gassing more than 2 ml/g with evidence of physical or chemical change).

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